

## First-principles calculations of defect energies in metals

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We review the self-consistent first-principles calculations for defect energies in metals, such as impurity-impurity, probe-impurity, and vacancy-impurity interaction energies. The calculations are based on the density-functional theory in the local-spin-density approximation (LSDA). The *non-local* effects beyond the LSDA are also examined using the generalized-gradient approximation. We also discuss the accuracy of the frozen-potential approximation which is practically needed for the calculation of interaction energies of complex systems, such as effective-pair interaction energies in random alloys.

### 1. INTRODUCTION

The knowledge of defect interactions in solids, such as impurity-impurity (I-I), probe-impurity (P-I), and vacancy-impurity (V-I) interaction energies, is indispensable for understanding many basic processes, such as diffusion, short-range order, segregation, ordering, *etc.* Królas *et al* successfully measured the interaction energies of impurities with probe atoms (<sup>99</sup>Rh, <sup>100</sup>Pd, <sup>111</sup>Ag, <sup>111</sup>In) in metals by use of perturbed angular correlation (PAC) experiments [1].

In the present paper we first review the present status of the calculations of point defect interaction in metals. The calculations apply the Korringa-Kohn-Rostoker (KKR) Green's function method for impurities and are based on the local-spin-density approximation (LSDA) of density-functional theory [2]. The *non-local* effects beyond the LSDA are also examined within the generalized-gradient approximation (GGA) proposed by Perdew and Wang [3]. We show in section 2 that the full self-consistent LSDA calculations based on the Kohn-Sham scheme reproduce reasonably well available experimental values for interaction energies [1] and that the contribution from the *non-local* effects mostly cancels out for P-I and I-I interactions except for V-I.

We next discuss the accuracy of the frozen-potential approximation (FPA), which may have its practical usefulness for complex systems which prohibit the full self-consistent treatment employed above due to computational or numerical problems. It is easily anticipated that the calculations of effective-pair interaction energies

in random alloys need huge computing times because the Kohn-Sham equation must be solved for many atomic arrangements with symmetry compared with systems such as point defects, at different average concentrations [2]. We assess its accuracy for two examples, exchange interaction energies (3.1) and interaction energies (3.2) of impurity dimers.

### 2. LSDA and GGA RESULTS of P-I and V-I PAIRS in Ag, Pd, and Rh

We note that in the present GGA calculations the *non-local* effects are taken into account only for the potentials in the impurity cluster [2], but not for the host Green's functions.

Figure 1 shows the calculated results for the interaction energies of P-I and V-I (I= 3*d* and 4*sp* impurities, P = In PAC probe) pairs in Ag, Pd, and Rh. The measured values obtained by Królas [1] are also shown, although with the exception of the In probe in Ag very few experimental results exist. It is noted that the chemical trends of available PAC results are reproduced reasonably by the LSDA calculations. The *non-local* effects, being the difference between LSDA (○, ●) and GGA (△, ▲) calculations, are very small (≤ 0.01 eV for most cases considered here) However, it is also seen in Fig. 1 that the *non-local* effects become quantitatively important for the V-I (I= 3*d* impurities) interaction energies. The increase of the contribution due to the *non-local* effects may be easily expected since the variation of 3*d* impurity charge density increases by the neighboring of a vacancy. The micromechanism of the chemical

trends of these interaction energies are already discussed [2,5]. We believe that the discrepancies between the calculated and measured values are probably due to the lattice relaxation effects neglected in the present approach since the same calculations reproduce almost exactly the experimental values for systems where impurities and hosts are located on the same row of the periodic table, such as those for 4*d* and 5*sp* impurities interacting with a In probe in Ag [2].

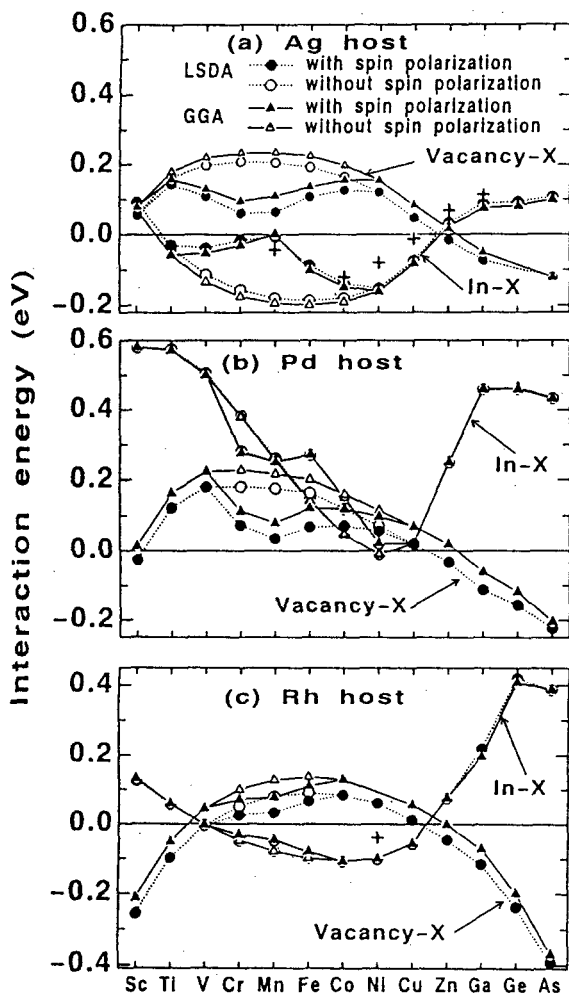


Figure 1. Calculated interaction energies of 3*d* and 4*sp* impurities with <sup>111</sup>In PAC probe in Ag(a), Pd(b), and Rh(c), based on the LSDA and GGA. The crosses (+) denote experimental values[1].

### 3. FROZEN-POTENTIAL APPROXIMATION

The purpose of this section is to clarify the accuracy of the frozen-potential approximation(FPA) [4] which may be useful for complex systems since it eliminates the need for self-consistency iterations by explicitly using the variational principle in the density-functional formalism and allows to calculate the total-energy changes only by use of the *band-energy* changes. We give the calculated results for the exchange interaction energies of 3*d* impurity dimers in Cu (in 3.1) and for the interaction energies of 3*d* and 4*sp* impurities in Cu and Ni (in 3.2). In the present work the frozen-potentials are determined by performing fully self-consistent calculations for single impurities in Cu and Ni; the potentials up to the nearest neighbors of impurities are determined self-consistently. All the calculations are based on the LSDA.

#### 3.1 Exchange interaction energies of 3*d* impurity dimers in Cu

Figure 2 shows the calculated results for the exchange interaction energies, defined as the difference between the total energy of anti-ferromagnetic,  $E_{AF}$ , and ferromagnetic,  $E_F$ , configurations. The self-consistent results are also shown for comparison. It is obvious from Fig. 2 that the FPA leads to nice agreement with the full self-consistent results. It may also be seen that the FPA works almost exactly for the weaker interaction at longer distances (see Figs. 2(c), 2(d)); the weaker the interaction is, the better the FPA. This may be expected because the FPA treats the total-energy differences accurately up to the first order of potential changes.

#### 3.2 Interaction energies of 3*d* and 4*sp* impurity dimers in Cu and Ni

Figure 3 shows the calculated results for the interaction energies. It is noted that the FPA reproduces reasonably well the chemical trends of the full self-consistent results although the quantitative agreements are not as good as for the exchange interaction energies; the difference for the dimer binding becomes large

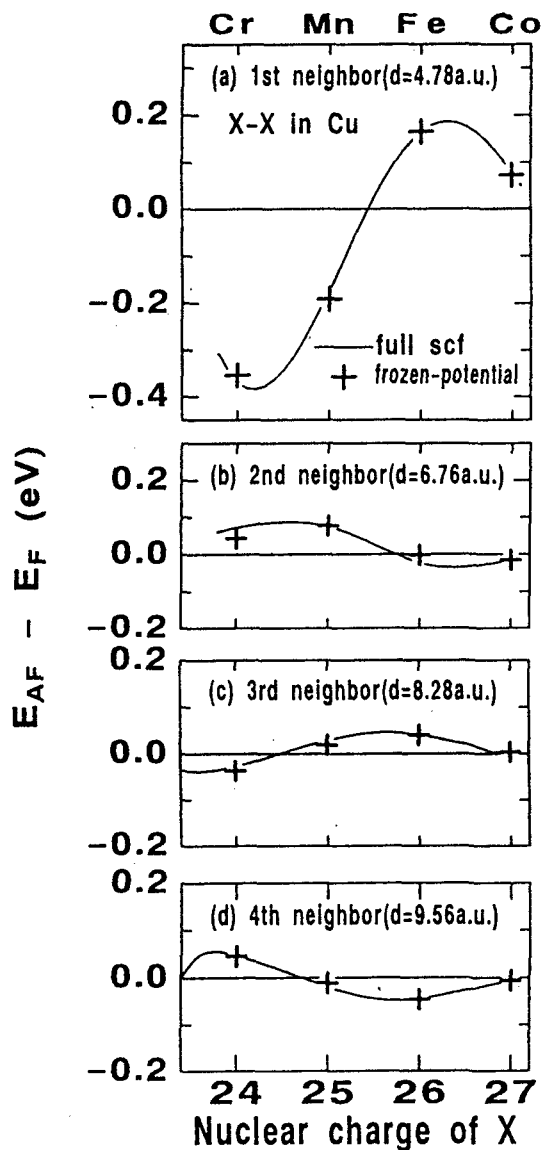


Figure 2. Calculated exchange interaction energies (+) of 3d impurity dimers in Cu, obtained by the frozen-potential approximation. The results up to 4-th neighbors are shown. The self-consistent results (full line) are also shown for comparison; the calculations have also been performed for noninteger nuclear charges.

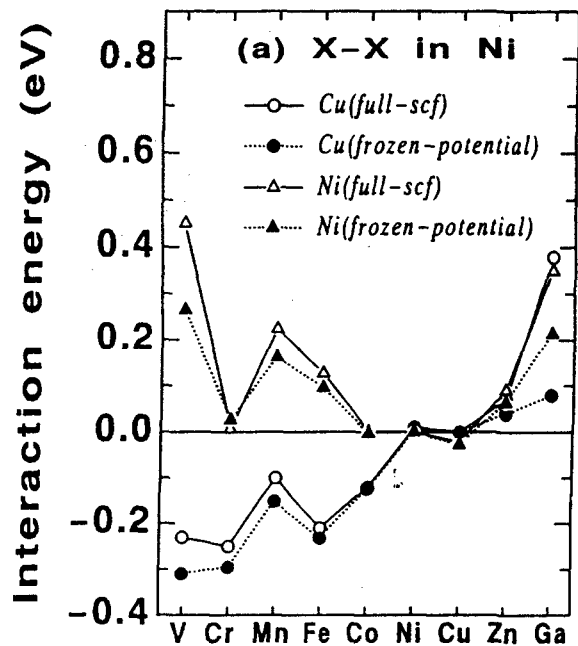


Figure 3. Calculated nearest-neighbor interaction energies (dotted line) of 3d and 5sp impurity dimers in Cu (●) and Ni(▲), obtained by the frozen-potential approximation. The fully self-consistent results (full line) are also shown for comparison.

for an early 3d impurity (V) and for 4sp impurities. The electrostatic energy (negative contribution) due to the charge transfer between the impurities and the neighboring host atoms, becomes also important for these impurities; it is seen that the interaction energies become more negative (attractive) by the FPA than by the full scf calculations since the charge transfer, causing the intercell electrostatic energy, is overestimated by the FPA. However it is also seen in Fig. 3 that the FPA works even quantitatively for the impurities (Cr, Mn, Fe, Co) located on neighboring positions of the host elements (Cu, Ni) in the periodic table. Presumably this result means that

the perturbation and charge transfer is small for these impurities. We also obtained similar results for  $4d$  and  $5sp$  impurity dimers in Pd and Rh. Thus we may conclude that the FPA may be useful for transition metal alloys of similar elements located on neighboring positions in the periodic table. This may justify the qualitative success of noniterative tight-binding calculations which have been used very often for the heats of formation of the transition-metal alloys [6]. The details, including the calculated results for  $4d$  and  $5sp$  impurity dimers in Pd and Rh as well as the interaction energies for longer distances, will be discussed elsewhere [7].

#### 4. CONCLUSION

We discussed the present status of first-principles calculations of defect interaction energies in metals. For the defect energies of the simple systems such as point defects the highly accurate full self-consistent calculations are now easily performed, as shown in the present paper. The lattice distortion effects, becoming important for the impurities with large lattice-misfit, are also under study [8]. On the other hand, for effective-pair interaction energies in random alloys, being configurationally averaged quantities, it is still difficult to carry through the full Kohn-Sham scheme because of huge computing times. In order to treat such complex systems we have examined the accuracy of FPA, one of the noniterative approaches which seem to be useful for the study of these systems. The calculations using the FPA for the random alloys are now in progress [2,9].

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